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One-Step Construction of Co₂P Nanoparticles Encapsulated into N-Doped Porous Carbon Sheets for Efficient Oxygen Evolution Reaction

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Abstract: It is critical and challenging to develop high performance transition metal phosphides (TMPs) electrocatalysts for oxygen evolution reaction (OER) to address fossil energy shortages. Herein, we report the synthesis of Co₂P embedded in N-doped porous carbon (Co₂P@N-C) via a facile one-step strategy. The obtained catalyst exhibits a lower overpotential of 352 mV for OER at a current density of 10 mA cm⁻² and a small Tafel slope of 84.6 mV dec⁻¹, with long-time reliable stability. The excellent electrocatalytic performance of Co₂P@N-C can be mainly owed to the synergistic effect between the Co₂P and highly conductive N-C substrate, which not only affords rich exposed active sites but also promotes faster charge transfer, thus significantly promoting OER process. This work presents a promising and industrially applicable synthetic strategy for the rational design of high performance nonnoble metal electrocatalysts with enhanced OER performance.

Keywords: cobalt phosphide; N-doped porous carbon; electrocatalyst; oxygen evolution reaction



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1. Introduction

As societies become further industrialized, fossil energy shortages have become a serious problem; the energy crisis, environmental pollution and the greenhouse effect are the main challenges facing the world in this century [1]. The high energy density, cleanliness and sustainability of hydrogen produced by the electrolysis of water make it one of the most promising substitutes for traditional fossil fuels [2]. In the overall water-splitting systems, oxygen evolution reaction (OER) acts as an anodic half-reaction, limiting the production of hydrogen in water splitting units due to its multi-step proton-coupled transfer process, which has slower kinetics than hydrogen evolution reaction (HER) [3,4]. To overcome this obstacle in OER, efficient catalysts are urgently required to facilitate OER kinetics and improve energy conversion efficiency [5]. Noble metal-based electrocatalysts such as RuO₂ and IrO₂ are the basic electrocatalysts used for OER, but the low material fractionation, high cost and lack of durability of noble metal oxides greatly limit their further industrial development [6,7]. For this reason, cheap and efficient non-precious metal electrocatalysts have been developed for overall water splitting, mainly transition metals and their oxides [8,9], transition metal sulfides [10,11], transition metal phosphides (TMPs) [12,13]. Among them, transition metal phosphides have received increasing attention due to their abundant reserves and low cost [14].

Depending on the type of phosphorus source and the reaction method, there are three general methods for the synthesis of TMPs. The liquid-phase reaction method uses organic phosphorus sources (TOP and TPP) as the phosphorus source [15,16]. The organic solvent

and the reaction temperature make the entire reaction system flammable and corrosive, and a continuous inert gas supply is required to ensure safety. The gas–solid reaction method uses hypophosphates (NaH_2PO_2 and $\text{NH}_4\text{H}_2\text{PO}_2$) as the phosphorus source, and the high-temperature heating of the phosphorus source will produce PH_3 highly toxic gas, which needs to be treated for toxic exhaust gas [17,18]. Pyrolytic reduction uses phosphates [19], polymetallic oxides [20], phytic acid [21], and other reagents with PO_4 groups as phosphorus sources. The PO_4 groups are easily complexed with metal ions, and under high temperatures and a reducing atmosphere, the P–O bonds break and combine with metal ions to form TMPs; however, the high temperature reaction makes it more energy intensive and limits large-scale preparation [22,23]. The complexity of the process and the high-risk factors hinder the practical production of TMPs.

Although TMPs have a good performance on OER, their inherent characteristics such as poor electrical conductivity and easy agglomeration limit the electrochemical kinetics and lead to reduced catalytic activity [24]. Forming a composite structure of TMPs with heteroatom-doped porous carbon materials is a practical solution to address the aforementioned issues [25]. For example, Sun and co-workers reported a series of transition metal phosphides encapsulated in nitrogen-phosphorus co-doped carbon, a carbon substrate that not only effectively enhances the catalytic performance of electrocatalysts, but also limits the growth and aggregation of nanoparticles [26]. It has been shown that porous carbon materials as a substrate can effectively disperse the TMPs to facilitate the exposure of active sites; in addition, the doping with heteroatoms such as nitrogen and phosphorus significantly improves the catalyst activity due to the synergistic effect [27]. To date, designing a low-cost, feasible and convenient method of coupling nanomaterials to carbon substrates for electrochemical catalysts remains a daunting task.

Herein, we report on the large-scale preparation of Co_2P nanoparticles encapsulated into N-doped porous carbon ($\text{Co}_2\text{P@N-C}$) by a facilitative one-step approach using glucose, phosphoric acid, urea and cobalt acetate as precursors. The synergistic effect between the cobalt phosphide nanoparticles and the N-doped carbon substrate results in remarkable catalytic properties. Additionally, it requires a low overpotential of 352 mV for OER to deliver a current density of 10 mA cm^{-2} under alkaline conditions. As well, the catalyst shows a negligible overpotential increase after 24 h stability test. Our work presents a promising and industrially accessible synthetic strategy for the rational design of high-performance catalysts.

2. Materials and Methods

2.1. Materials

Cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.5%), D-(+)-Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, 99.5%), Urea ($\text{CO}(\text{NH}_2)_2$, 99.5%), and phosphoric acid (H_3PO_4 , 85 wt%) were purchased from Aladdin Reagents Ltd., Shanghai, China. All reagents were of analytical grade and required no further purification. All experiments used deionized water (DIW). The commercial RuO_2 (99.9%) catalyst was bought from Sigma-Aldrich, St. Louis, MI, USA.

2.2. Synthesis of $\text{Co}_2\text{P@N-C}$

Typically, 3 g of urea, 1 g of glucose and 0.1 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 35 mL of DIW at room temperature, then 10 μL of phosphoric acid was added with continuous stirring for 30 min. Next, the precursor was heated at 85°C for 4 h to remove moisture, then placed in a quartz tube and annealed at 900°C for 1 h in an NH_3 atmosphere at a heating rate of 5°C min^{-1} . After cooling down to room temperature, the obtained black powder was $\text{Co}_2\text{P@N-C-900}$. For comparison, $\text{Co}_2\text{P@N-C-800}$ and $\text{Co}_2\text{P@N-C-1000}$ were synthesized by the same procedure, except for the pyrolysis temperatures of 800°C and 1000°C , respectively.

2.3. Electrochemical Measurement

All the electrochemical measurements were performed on a CHI760E electrochemical workstation in a standard system at room temperature. A glass carbon electrode (GCE), a graphite electrode and a saturated calomel electrode (SCE) served as the working electrode, counter electrode and reference electrode, respectively. Typically, 5 mg of the sample was dispersed in a mixture of 400 μL water and 80 μL ethanol with 20 μL Nafion solution, and then the mixture was under continuous ultrasonication for 30 min to obtain a homogenous ink. Then, 8 μL of the catalyst ink was loaded on the glass carbon electrode, resulting in a catalyst loading of 0.64 mg cm^{-2} (GCE: 4 mm in diameter). Polarization data were obtained at a scan rate of 5 mV s^{-1} in 1.0 M KOH. In all electrochemical measurements, all potentials were referenced to the reversible hydrogen electrode (RHE) by the equation $E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \text{ pH} + 0.241$. The electrochemical impedance spectroscopy (EIS) was carried out in the range of 10^5 to 0.01 Hz under a current signal amplitude of 5 mV. The stability tests were measured by cyclic voltammetry with 2000 scans (CV, sweep frequency, 200 mV s^{-1}) and long-term chronoamperometry.

3. Results and Discussion

3.1. Design and Characterizations of Catalysts

A one-step gelation method and subsequent thermal treatment were used to prepare Co_2P nanoparticles encapsulated in N-doped carbon ($\text{Co}_2\text{P@N-C}$) from urea and glucose (C, N source), phosphoric acid (P source) and cobalt (Co source), respectively (Figure 1). In brief, the light pink gel precursor was synthesized by heating and stirring glucose, phosphoric acid, urea and cobalt acetate. Then the precursor was annealed under an NH_3 atmosphere. During the annealing process, the evaporation of water molecules creates a porous form for the carbon substrate and the ammonia produced by the decomposition of urea causes the carbon substrate to be doped with nitrogen. In addition, the partial P source in phosphoric acid forms cobalt phosphide particles with the Co source, resulting in particles embedded in N-doped porous carbon due to the limitations of the carbon substrate. To investigate the effect of different temperatures on the morphology and properties of the catalysts, $\text{Co}_2\text{P@N-C}$ samples were obtained at 800°C and 1000°C , respectively.

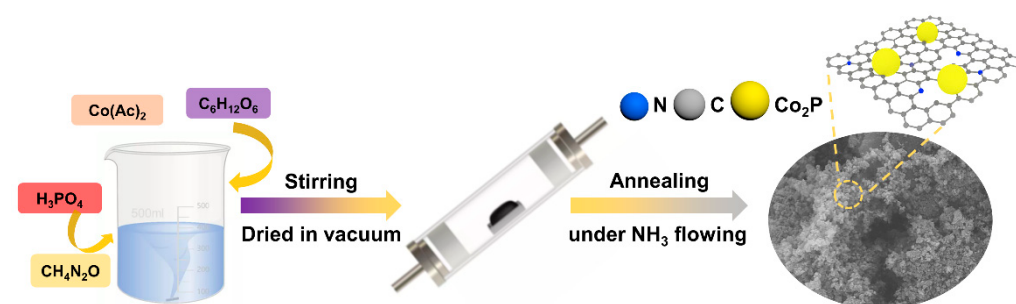


Figure 1. Schematic of the synthesis of $\text{Co}_2\text{P@N-C}$.

The morphology was examined by scanning electron microscopy (SEM). Figure 2a shows a low magnification SEM image of $\text{Co}_2\text{P@N-C-900}$, showing a fluffy porous structure with a large specific surface area exposing multiple active sites for OER process. More importantly, $\text{Co}_2\text{P@N-C-900}$ can be easily scaled up (inset of Figure 2a). Figure 2b further shows that these nanoparticles are immobilized on porous carbon and surrounded by pore space. To explore the effect of different temperatures on morphology, $\text{Co}_2\text{P@N-C-800}$ and $\text{Co}_2\text{P@N-C-1000}$ samples consist of amorphous particles with uneven distribution. (Figure S1). The transmission electron microscopy (TEM) image shown in Figure 2c demonstrates the Co_2P nanoparticles with an average diameter of 65 nm are homogeneously confined within the carbon layers. The detailed structural information of these particles is demonstrated by high-resolution TEM (HRTEM) images shown in Figure 2d,e. The surface of the Co_2P nanoparticle with a crystalline surface spacing of 0.209 nm is covered with

an amorphous carbon layer, corresponding to the (211) crystalline surface of Co_2P ; this core-shell structure facilitates the acceleration of electron transfer in the catalytic process. Due to the unique core-shell encapsulation of $\text{Co}_2\text{P}@N\text{-C-900}$, it efficiently prevents the agglomeration and corrosion of Co_2P nanoparticles during OER and consequently endows its excellent durability and stability. Figure 2f depicts the selected area electron diffraction (SAED) pattern, which further confirms the successful synthesis of Co_2P . In addition, element mapping images confirm the presence of Co_2P nanoparticles and the homogeneous distribution of N elements in the porous carbon substrate (Figure 2g and Figure S2). All these results convincingly suggest that the Co_2P nanoparticles are successfully synthesized and uniformly anchored in N-doped porous carbon.

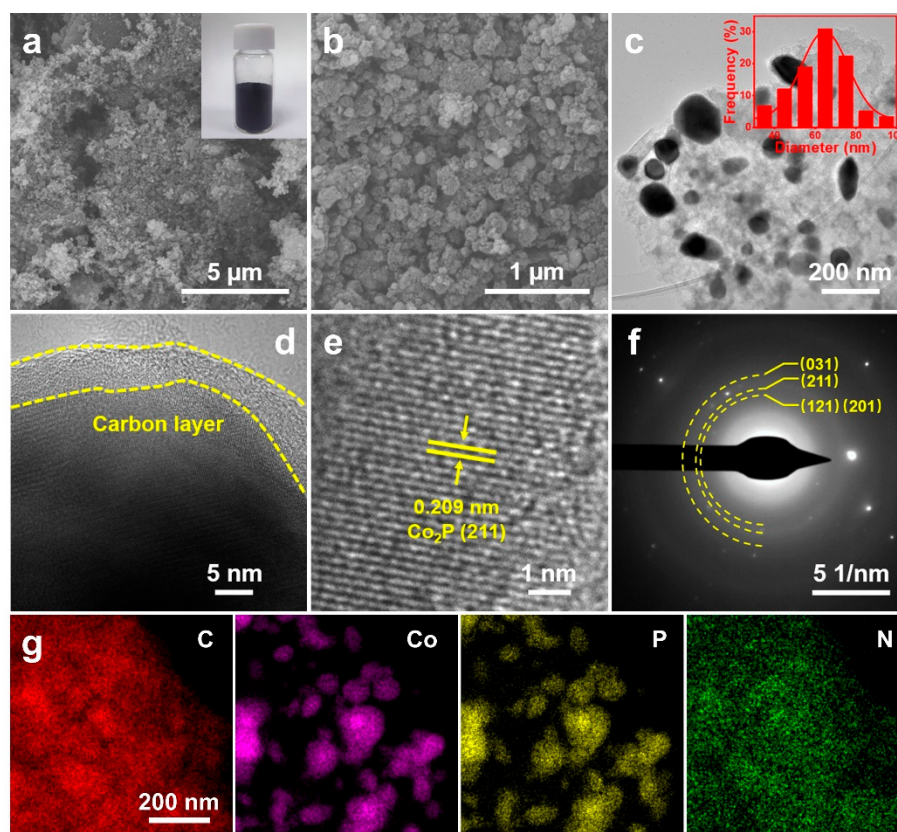


Figure 2. The morphology and structure of the $\text{Co}_2\text{P}@N\text{-C-900}$. (a,b) SEM images (inset digital photo shows the production of $\text{Co}_2\text{P}@N\text{-C-900}$ in the gram scale), (c) TEM (inset shows particle size distribution of $\text{Co}_2\text{P}@N\text{-C-900}$) and (d,e) HR-TEM images, (f) SAED pattern, and (g) elemental mapping images of $\text{Co}_2\text{P}@N\text{-C-900}$.

To identify the structure of the materials, X-ray powder diffraction (XRD) measurements were performed. XRD patterns of various $\text{Co}_2\text{P}@N\text{-C}$ obtained by synthesis at different temperatures are presented in Figure 3a. The $\text{Co}_2\text{P}@N\text{-C}$ composite material has four obvious diffraction peaks at 40.7° , 40.9° , 43.3° and 48.7° corresponding to the (121), (201), (211) and (031) planes of the orthorhombic Co_2P , respectively, while the broad peak at 25.8° is attributed to the (002) graphite plane. The crystalline planes (121), (201), (211) and (031) correspond to lattice spacings of 0.221 nm, 0.220 nm, 0.209 nm and 0.187 nm, where the (211) plane is consistent with the HRTEM in Figure 2e. The specific surface area and pore size distribution of $\text{Co}_2\text{P}@N\text{-C}$ were obtained by N_2 adsorption-desorption isotherm (Figure 3b). The curves clearly show a type IV hysteresis loop demonstrating the presence of a large number of mesopores in $\text{Co}_2\text{P}@N\text{-C-900}$. The BET surface areas of $\text{Co}_2\text{P}@N\text{-C-800}$, $\text{Co}_2\text{P}@N\text{-C-900}$ and $\text{Co}_2\text{P}@N\text{-C-1000}$ are 148, 338 and $40 \text{ m}^2 \text{ g}^{-1}$. Moreover, the average pore size of $\text{Co}_2\text{P}@N\text{-C-900}$ is 4 nm (Figure S3). This mesoporous morphology of $\text{Co}_2\text{P}@N\text{-C-900}$ may offer an efficient diffusion pathway and more electroactive sites,

thus facilitating the enhancement of the catalytic process. To further analyze the degree of graphitization and the defect level for Co₂P@N-C, the Raman spectrum of the samples prepared at different heating temperatures is recorded (Figure 3c). The defect-induced (D) band located at about 1340 cm⁻¹ and the graphitic-induced (G) band at about 1583 cm⁻¹ yield an I_D/I_G intensity ratio. The intensity ratio I_D/I_G of Co₂P@N-C-900 is about 1.06, is higher than Co₂P@N-C-800 (1.02) and Co₂P@N-C-1000 (0.97), reflecting that there are more defects and disordered structures in Co₂P@N-C-900.

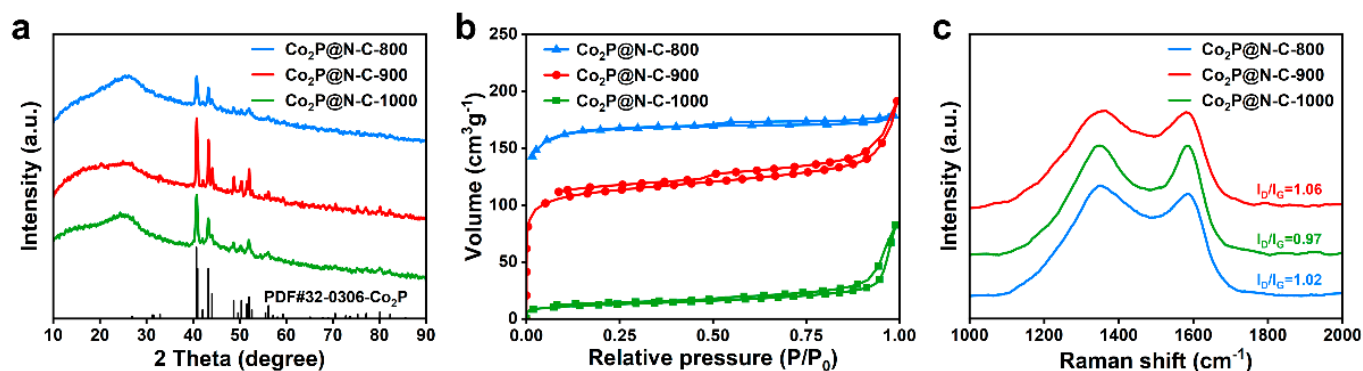


Figure 3. (a) XRD spectra of samples calcined at different temperatures. (b) Nitrogen (N₂) adsorption/desorption isotherm of Co₂P@N-C-800, Co₂P@N-C-900 and Co₂P@N-C-1000. (c) Raman spectroscopy of Co₂P@N-C-800, Co₂P@N-C-900 and Co₂P@N-C-1000.

X-ray photoelectron spectroscopy (XPS) analysis was performed to examine the valence states and surface chemical composition of Co₂P@N-C-900. The survey XPS spectra reveal that Co₂P@NPC-900 consists of C, N, Co and P elements (Figure S4). To further explore the bonding structure, high-resolution XPS spectra were also gained. As illustrated in Figure 4a, the C 1s spectrum has three peaks at 284.7, 285.6 and 287.9 eV, which can be corresponded to C-C/C=C, C-N/C-O and C=O, respectively [28]. The existence of the N-doped carbon skeleton improves the porousness and electronegativity of the whole composite. Rapid contact between the electrolyte and active sites provides a shorter pathway for charge transfer. The high-resolution Co 2p spectrum shows four main peaks at 778.4, 781.6, 797.2 and 801.6 eV, which are characteristic of Co 2p_{3/2} and Co 2p_{1/2}. Among them, the peaks located at 778.4 and 797.2 eV correspond to metallic Co-P in Co₂P. The peaks centered at 778.4 and 797.2 eV correspond to Co 2p_{3/2} and Co 2p_{1/2} of Co³⁺, while the peaks at 781.6 and 801.6 eV can be assigned to Co²⁺. Meanwhile, the peaks observed at 781.6 and 801.6 eV, both with obvious satellite peaks (denoted as Sat.), are assigned to oxidized Co species (Figure 4b) [29]. The high-resolution N 1s spectrum is provided in Figure 4c. It can be deconvoluted into four peaks at 398.0, 398.8, 400.9 and 402.3 eV, corresponding to pyridinic N, pyrrolic N, graphitic N and oxygenated N, respectively [30]. It was previously reported that N-doping can modulate the electronic structure of its neighboring C atoms, improving the electrical conductivity of the carbon obtained and synergistically inducing the creation of a large number of deficiencies in the carbon, thus further enhancing its electrocatalytic performances [31]. The binding energies of P 2p peaks located at 129.7 and 130.5 eV correspond to P 2p_{3/2} and P 2p_{1/2} in Co₂P while the broad peak at 133.4 eV belongs to P-O [32]. These spectroscopic analyses agree well with the aforementioned results, further confirming the formation of Co₂P nanoparticles on the porous carbon substrate.

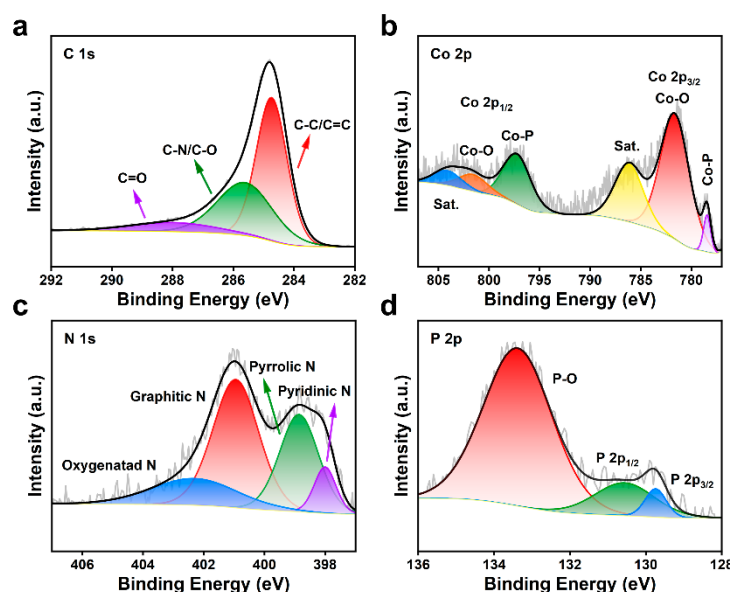


Figure 4. High-resolution XPS spectrum (a) C 1s, (b) Co 2p, (c) N 1s and (d) P 2p of Co₂P@N-C-900.

3.2. Electrocatalytic Performances

The electrocatalytic OER performance of Co₂P@N-C and commercial RuO₂ catalysts was investigated in 1.0 M KOH solution using a typical three-electrode system. Obviously, the linear sweep voltammetry (LSV) polarization curves in Figure 5a show that Co₂P@N-C-900 performs with a small overpotential of 353 mV for reaching a current density of 10 mV cm⁻² as compared with Co₂P@N-C-800 (417 mV) and Co₂P@N-C-1000 (409 mV), and is even better than commercial RuO₂ (375 mV). The overpotential of Co₂P@N-C-900 also outperforms many recently reported noble metal-free OER electrocatalysts (Table S1). Figure 5b shows the Tafel plots based on LSV polarization curves. The Tafel slope of Co₂P@N-C-900 is 84.6 mV dec⁻¹, which is close to that for RuO₂ (79 mV dec⁻¹), and lower than those of Co₂P@N-C-800 (87.3 mV dec⁻¹), indicating the higher catalytic kinetics of Co₂P@N-C-900 for the OER process. Interestingly, Co₂P@N-C-1000 has the smallest Tafel slope (65.5 mV dec⁻¹), which can be attributed to the increased conductivity of the carbon substrate due to the pyrolysis temperature. In addition, electrochemical impedance spectroscopy (EIS) was performed to explore the reaction kinetics (Figure 5c and Table S2) [33]. From the Nyquist plots, the charge transfer resistance (R_{ct}) of Co₂P@N-C-900 is found to be the smallest among the control samples under the same conditions, demonstrating that the kinetics for OER is much faster. Furthermore, cyclic voltammetry (CV) measurements were carried out to determine the electrochemically active surface area (ECSA) at different scan rates (Figure S5). As exhibited in Figure 5d, the calculated double-layer capacitance (C_{dl}) values for Co₂P@N-C-900 is 16 mF cm⁻², which is much larger than those of 1.9 and 2.4 mF cm⁻² for Co₂P@N-C-800 and Co₂P@N-C-1000, respectively. Such a high value of C_{dl} value indicates that the Co₂P@N-C-900 catalyst with a large ECSA favors the exposure of the active site to the OER. Stability is another important indicator to evaluate whether catalysts have the potential for industrial application. The polarization curves of Co₂P@N-C-900 presented in Figure 5e display a negligible loss of activity after 2000 CV cycles. Furthermore, the current–time curve further demonstrates that Co₂P@N-C-900 exhibits a stable current density of 10 mA cm⁻² for 24 h, verifying good long-term stability. Based on the above results, Co₂P@N-C-900 could be used as a powerful and high-efficiency electrocatalyst for highly active OER reactions.

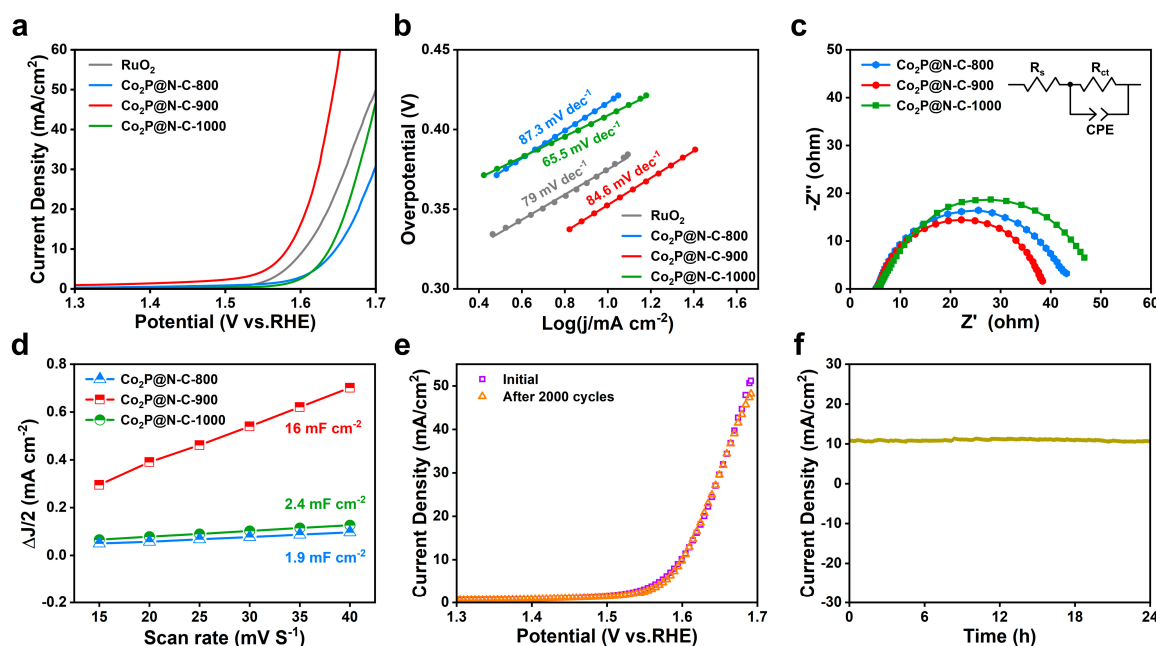


Figure 5. (a) OER polarization curves and (b) corresponding Tafel plots of $\text{Co}_2\text{P@N-C-800}$, $\text{Co}_2\text{P@N-C-900}$, $\text{Co}_2\text{P@N-C-1000}$ and commercial RuO_2 in 1 M KOH. (c) Nyquist plots and (d) variation of double layer charging currents as a function of scan rate of $\text{Co}_2\text{P@N-C-800}$, $\text{Co}_2\text{P@N-C-900}$ and $\text{Co}_2\text{P@N-C-1000}$. (e) Stability of $\text{Co}_2\text{P@N-C-900}$ electrocatalysts before and after 2000 cycles in 1.0 M KOH. (f) Time-dependent current density curves for $\text{Co}_2\text{P@N-C-900}$ at the constant potential for 24 h.

4. Conclusions

In summary, we have successfully fabricated Co_2P nanoparticles embedded in N-doped porous carbon via a one-step pyrolysis strategy. The heteroatom-doped carbon layers provide physical and chemical protection for the Co_2P nanoparticles in alkaline electrolytes. Thanks to the large surface area and mesoporous morphology of $\text{Co}_2\text{P@N-C-900}$, which can facilitate the penetration of the electrolyte and reduce electron/ion diffusion pathways and maximize the exposure of active sites, the as-prepared $\text{Co}_2\text{P@N-C-900}$ exhibits outstanding OER performance. It only requires an overpotential of 352 mV to afford 10 mA cm^{-2} , which is better than those of recently reported noble metal-free catalysts. Meanwhile, it also shows superior long-term stability for 24 h. Furthermore, we have demonstrated that our synthesis strategy can be easily scaled up for large-scale industrial production. This work provides a facile, promising and cost-effective strategy to prepare highly active catalysts for various energy storage and conversion applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16010478/s1>, Figure S1: SEM images of (a) $\text{Co}_2\text{P@N-C-800}$ and (b) $\text{Co}_2\text{P@N-C-1000}$; Figure S2: Low magnification HAADF-STEM image of $\text{Co}_2\text{P@N-C-900}$; Figure S3: Pore size distribution plot of $\text{Co}_2\text{P@N-C-900}$; Figure S4: XPS survey spectra of $\text{Co}_2\text{P@N-C-900}$; Figure S5: CV curves of $\text{Co}_2\text{P@N-C}$ catalysts in the non-Faradaic region (1.05–1.35 V) were obtained at different scanning rates. (a) $\text{Co}_2\text{P@N-C-800}$, (b) $\text{Co}_2\text{P@N-C-900}$ and (c) $\text{Co}_2\text{P@N-C-1000}$; Table S1: Comparison of OER performance of $\text{Co}_2\text{P@N-C-900}$ with other recently reported electrocatalysts in alkaline electrolyte [34–42]; Table S2: EIS calculation parameters of $\text{Co}_2\text{P@N-C-900}$ and other samples for OER.

Author Contributions: Conceptualization, R.Z.; Formal analysis, Y.L.; Investigation, Y.G.; Data curation, K.W. and Y.T.; Writing—original draft, K.W.; Writing—review & editing, P.W.; Supervision, X.W.; Project administration, P.W. and Z.L.; Funding acquisition, Z.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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